REMARKS:

Claims 1-9 are pending in the application. Claims 8-9 are withdrawn. Claim 1 is independent. No claims are amended, deleted, or added in this reply. Applicants respectfully request reconsideration of the present application.

Amendment of Specification

The foregoing amendment of the specification merely corrects a typographical error and introduces no new material.

Rejection under 35 U.S.C. § 103(a):
References do not teach or suggest all of the claim limitations

Claims 1-7 stand rejected as being obvious under 35 U.S.C. § 103(a) over either JP 60-248,854 ('854) or JP 55-73,448 ('448). Applicants submit that the Office Action fails to establish a *prima facie* case of obviousness. See, e.g., MPEP § 2142. The Office Action asserts that each of the prior art references substantially show the invention as claimed; yet the Office Action also concedes that "the rotation speed of the rolls, the gap of the nip, the melt temperature and surface temperature of the rolls" are not shown. Prior art references must teach or suggest all of the claim limitations. See MPEP § 2143. The references cited by the Examiner do not teach or suggest all of the methods and limitations of the claimed invention.

For instance, neither reference teaches or suggests "the rotation rate of the two rolls is in the range of 1 to 10 cm/sec" as claimed in the present invention. Only the abstract of reference '854 discloses a rotation rate, and it teaches away from this rate by orders of magnitude, disclosing a rotational rate of 3,000 rpm and roll outer diameter of 200mm. The sole appearance of "rpm" in the Japanese text of reference '448 apparently discloses 2,700 rpm. Upon conversion from revolutions per minute to centimeters per second, the rotational rate taught by '854 is:

1358858_1

$$\pi \times 200 \text{ mm} \times 3,000 \text{ rpm} \div 60 \text{ s/m} \div 10 \text{ mm/cm} \cong 3,142 \text{ cm/s}.$$

Such a rate does not teach or suggest the claimed rate and does not make the claimed rate

obvious. As noted in paragraphs [0036] and [0051] of the current application, if the rotation

rate of the two rolls "is too fast, uniform cooling is not sufficiently accomplished, and thus, it

is difficult to produce a sheet with high quality." Further, rotational rates greater than the

claimed range may not produce bulk amorphous alloy sheets at all. See the highlighted

portion of the paper, Lee, et al. (some authors are present Applicants), *Sheet fabrication of*

bulk amorphous alloys by twin-roll strip casting, 53 Scripta Materialia 693, 695, (2005),

enclosed herewith.

Additionally, neither '854 nor '448 teach or suggest a method for producing a bulk

amorphous alloy sheet as claimed and as defined in paragraph [0054] of the instant

specification:

> an amorphous alloy of the present invention is processed into a material
> which has structural continuity and a relatively large two- or three-
> dimensional dimension, not into a thin film (of <u>100 μm or less</u> in
> thickness, for example) dimension. For example, an amorphous alloy
> sheet of the present invention may have a thickness of about <u>0.5 to 20 mm</u>,
> but is not limited thereto. (emphasis added)

In contrast, the abstract of '854 teaches that a <u>30 μm thick</u>, 2 cm wide "thin strip" is

produced using the disclosed cooling roll. The abstract of reference '448 discloses a "ribbon"

of unstated dimension. Thus, both references teach or suggest merely thin film alloy strips or

ribbons and neither suggests nor teaches a "gap between the two rolls [] in the range of 0.5 to

20 mm", as claimed, producing a bulk amorphous alloy sheet having a thickness in the range

of 0.5 to 20 mm. The references are directed to thin film production methods unsuitable for

production of a bulk amorphous alloy sheet; see, e.g., paragraph [0063] (exemplary bulk

amorphous alloy sheet 2 mm thick, 10 cm wide, 1 m long).

Furthermore, the Examiner has pointed to no disclosure in '854 or '448 which teaches

1358858_1

or suggests "cooling the melt at a cooling rate higher than the critical cooling rate for transformation of the melt into an amorphous solid phase, when the melt passes through the gap defined between the two rolls" as claimed in the present invention. Reference '854 claims a cooling roll. Reference '448 discloses a melt spouting method.

Neither reference teaches or suggests two rolls, "each of which is provided with heat exchange means." The Examiner, with apparent reference to claims 3 and 4, asserts that it is conventional to "use a coolant for cooling the copper cast roll" but does not provide a reference disclosing this convention, nor does the Examiner identify a teaching or suggestion to use a heat exchange means (with or without a coolant) in combination with the other claimed features of the present invention.

Additionally, the Examiner does not address the specific limitations of each of the dependent claims rejected.

For at least the foregoing reasons, the present claims are patentable over the cited references.

Rejection under 35 U.S.C. § 103(a):
References are not enabled

Furthermore, the references cited by the Examiner are not enabled. "To render a later invention unpatentable for obviousness, the prior art must enable a person of ordinary skill in the field to make and use the later invention." *Beckman Instruments, Inc. v. LKB Produkter AB*, 892 F.2d 1547, 1551 (Fed. Cir. 1989); cited by *In re Kumar*, 418 F.3d 1361 (Fed. Cir. 2005). The Examiner asserts that "rotation speed of the rolls, the gap of the nip, the melt temperature and surface temperature of the rolls ... depend on the particular amorphous alloy to be processed and would have been obvious to obtain ... through routine experimentation." However, the Examiner cites no evidence that such experimentation would have been routine and is applying impermissible hindsight. The present application discloses many difficulties

1358858_1

precluding a conclusion of "routine experimentation." See, for example, paragraphs [0034] (problems with melt temperature), [0035] (problems with roll surface temperature) and [0036] (problems with rotation rate). The references cited by the Examiner relate only to thin film amorphous alloy production and do not enable one of skill in the art to discover a method for producing a bulk amorphous alloy sheet, even with routine experimentation.

Rejection under 35 U.S.C. § 103(a): Secondary Considerations

Applicants also direct the Examiner's attention to secondary considerations regarding obviousness. "Recognition of need, and difficulties encountered by those skilled in the field, are classical indicia of unobviousness." *In re Dow Chemical Co.*, 837 F.2d 469 (Fed. Cir. 1988). There has been increasing interest in amorphous alloy sheets; demands in various industrial fields for efficient and industrially applicable methods to mass-produce amorphous alloy sheets have gone unsatisfied (para. [0006]). Strip casting processes were understood to be unsuitable or improbable for production of an amorphous alloy sheet (para. [0009]). The present invention provides methods for producing bulk amorphous alloy sheets with high quality at low production costs (paras. [0011], [0067]), thus satisfying a long felt need.
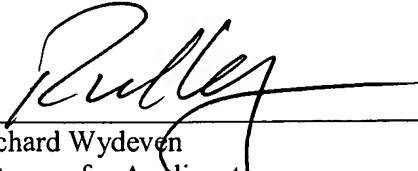
Conclusion

All of the stated grounds of rejection have been properly traversed. Applicants therefore respectfully request that the Examiner reconsider all presently outstanding rejections, and that they be withdrawn. Applicants believe that a full and complete reply has been made to the outstanding Office Action and, as such, the present application is in condition for allowance.

If the Examiner believes that a telephone conference or personal interview would expedite passage of this application to issue, the Examiner is invited to call the undersigned at the number below.

1358858_1

If any extension of time is required in connection with the filing of this paper and has

not been requested separately, such extension is hereby requested.

The Commissioner is hereby authorized to charge any fees and to credit any

overpayments that may be required by this paper under 37 C.F.R. §§ 1.16 and 1.17 to Deposit

Account No. 02-2135.

Respectfully submitted,

Date: _Oct. 26, 2006_ By _____

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1358858_1

Sheet fabrication of bulk amorphous alloys by twin-roll strip casting

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Abstract

Twin-roll strip casting has been utilized to fabricate the sheet products of bulk amorphous alloys. Simulation of solidification behavior and actual twin-roll strip casting show that the optimum casting conditions are such that the alloy is in supercooled liquid state at roll nip area rather than fully amorphized.
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Keywords: Bulk amorphous materials; Sheets; Casting; Simulation

1. Introduction

The bulk amorphous alloys have excellent strength and corrosion resistance, which are quite attractive for structural applications [1–6]. Despite such remarkable properties, however, there are several drawbacks that prevent their widespread commercialization and application. One is that bulk amorphous alloys generally suffer from a lack of plasticity, making them prone to catastrophic failure in load-bearing applications. Recent development of new multicomponent alloys incorporating crystalline particles within an amorphous matrix has shown a promise for improved plasticity [7,8]. The other drawback is that the size and shape of bulk amorphous alloy products are quite limited since the only commercially available process for their fabrication is die-casting. There is no fabrication method available which can continuously produce sheet or plate products of bulk amorphous alloys. Considering that flat rolled products such as sheets and plates share more than 80% of metals and alloys products, continuous fabrica-

tion of bulk amorphous alloys in sheet form would greatly expand their applications.

Here, we applied the twin-roll strip casting process for continuous fabrication of bulk amorphous alloy sheets. In twin-roll strip casting process, molten metal is fed through two water-cooled rotating rolls. As the molten metal contacts with rolls, there is a formation of solidified shell near the contact region between melt and rolls. At the same time, its thickness is reduced by the rolling action of the rotating rolls. This twin-roll strip casting process has several advantages over conventional sheet making processes [9–13]. Since it combines casting and hot rolling into a single operation, it reduces production costs and energy, and requires low capital investment when compared to conventional processes. Twin-roll strip casting also offers the much reduced cooling rate over conventional continuous or direct chill casting. Previous studies on twin-roll strip casting of Al and Mg alloys [9–11] show that cooling rates of 10^2–10^3 K/s can be achieved, which might be enough for the formation of amorphous structure by twin-roll strip casting. Such characteristics of twin-roll strip casting appear to be suitable for the production of bulk amorphous alloy sheets. However, bulk amorphous

forming alloys generally have much lower thermal conductivities than conventional alloys [14], and therefore high enough cooling rates might not be achieved during twin-roll strip casting to form amorphous structure.

2. Simulation of solidification behavior during twin-roll strip casting

During the twin-roll strip casting of bulk amorphous forming alloys, amorphization or crystallization can occur depending on the cooling rates and thermal behavior experienced. Thermal behavior during twin-roll strip casting has been simulated with FLUENT to gain an insight into phase transformation behavior of bulk amorphous forming alloys. The basic assumptions used for simulation were as follows: (1) the ratio of the width to thickness is quite large to neglect the side board effect, (2) the process is in a steady state, i.e., the process itself is in a continuous mode and the melt is supplied and delivered from the rolls at a constant rate, (3) the flow is laminar, which means that there is little or no mixing of the melt across the "boundaries" of each layer as the melt flow proceeds through the path, and (4) vitrification of amorphous alloys is regarded as the continuous transformation (i.e., continuous increase in viscosity with decreasing temperature from the liquid phase) different from solidification of conventional crystalline alloys. Assuming the symmetry, only the upper half part of the roll gap area of the horizontal strip caster was considered. For the reliable results, relatively denser grid system was applied near the roll surface and 40 and 15 grids are used in x and y directions, respectively. It was assumed that the volume per unit time of the injected sheet was same as that of poured melts and the casting speed was same as the resolving speed of the roll.

Zr-base amorphous forming alloy (Vit-1 alloy) with a nominal composition of $Zr_{41.2}Ti_{13.8}Cu_{12.5}Ni_{10.0}Be_{22.5}$ was chosen for the simulation study since among various bulk amorphous forming alloys it is the only alloy having all the physical property values needed for calculation. The physical properties of the Vit-1 alloy and the inlet parameters used in simulation are shown in Table 1. Values of viscosity and specific heat as a function of temperature are obtained from the literature [15]. Since the value of the heat transfer coefficient is not available, it was estimated from the literatures on melt infiltration casting [16] and twin-roll strip casting of stainless steels [17–20].

Fig. 1 shows the typical solidification simulation results when the heat transfer coefficient is 3000 $W/m^2 K$. It can be seen from Fig. 1 that the rotating speed of rolls has a significant effect on temperature profile of the sheet. When the rotating speed is 1 rpm (0.6 m/min), the temperature of the sheet reaches T_g (630 K) well before the sheet passes the roll nip area. On the other hand, the sheet is still in supercooled liquid state when the rotating speed is 3 rpm (1.9 m/min). In

Table 1
Physical properties of the Vit-1 alloy and inlet parameters

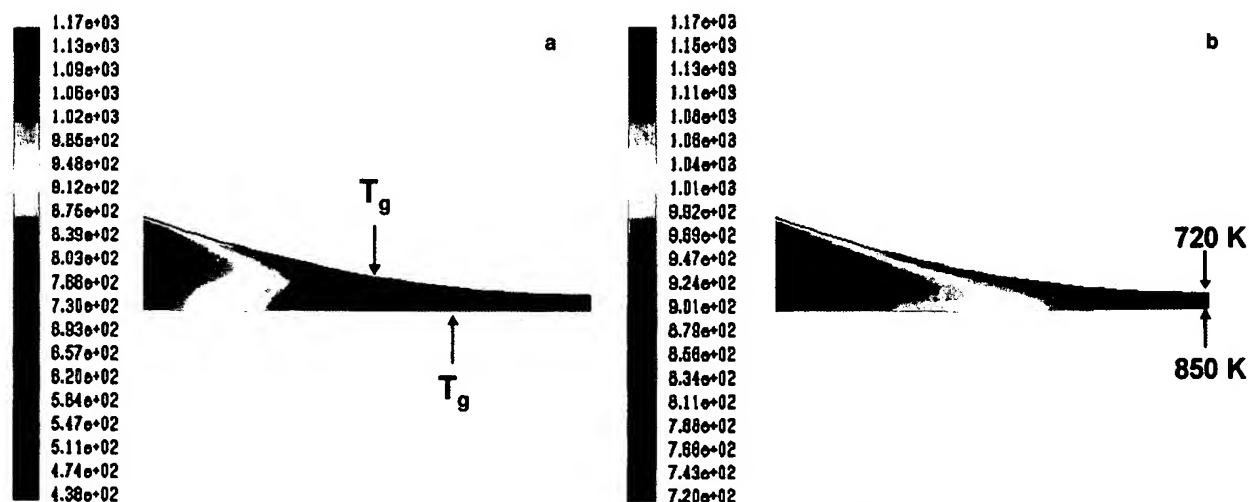| Physical properties of the Vit-1 alloy		Inlet parameters	
Liquidus temp.	993 K	Roll diameter	200 mm
Glass transition temp.	630 K	Roll gap	2 mm
Density	6100 kg/m^3	Temp. of rolls	300 K
Viscosity	Ref. [15]	Rotating speed of rolls	1, 3 and 5 rpm
Specific heat	Ref. [15]	Initial melt temp.	1173 K
Thermal conductivity	4 W/m K	Heat transfer coefficient	1000–5000 W/m^2 K

Fig. 1. Simulation results showing the temperature distribution near roll gap area; (a) rotating speed of 1 rpm and (b) rotating speed of 3 rpm.

this case, the surface and mid-thickness temperatures of the sheet reach about 720 K and 850 K, respectively, at the roll nip area. At a faster rotating speed (e.g., 5 rpm), the sheet is still in liquid state at the mid-thickness region. These simulation results indicate that the formation of amorphous structure is basically possible by twin-roll strip casting and optimum twin-roll strip casting conditions can be identified based on these results. However, there are some critical issues that should be addressed prior to the actual application of twin-roll strip casting for fabricating bulk amorphous alloy sheets.

When the alloy becomes fully amorphous before it passes the roll nip area (e.g., at rotating speed of 1 rpm), the injection of the alloy from the roll nip point might not be possible since the thickness of the fully amorphous sheet could not be reduced due to its very high strength. On the other hand, if the alloy is in super-cooled liquid state before it passes the roll nip area (e.g., at rotating speed of 3 rpm), the formation of amorphous structure through the thickness of the sheet might not be possible since the temperature of the alloy is still well above T_g. Considering the contact time (1 s) of the alloy with the roll surface and the rotating speed of the rolls, the cooling rates of the alloy at the surface and the mid-thickness region at the roll nip area have been calculated to be about 470 K/s and 330 K/s, respectively. These values are compared with the critical cooling rate (R_c) of the Vit-1 alloy to form amorphous structure [15,21,22] (Fig. 2). As shown in Fig. 2, the cooling rates of the alloy at the rotating speed of 3 rpm are much faster than the R_c (about 1 K/s) of the Vit-1 alloy and the final temperatures of the alloy at the roll nip area have fallen below the nose temperature of the CCT diagram, suggesting that amorphous structure can form through the thickness of sheet although the temperature of the alloy at roll nip area is well above T_g. Although the sheet will be air cooled after injection from the roll nip area, the alloy would hardly be crystallized since the crystalli-
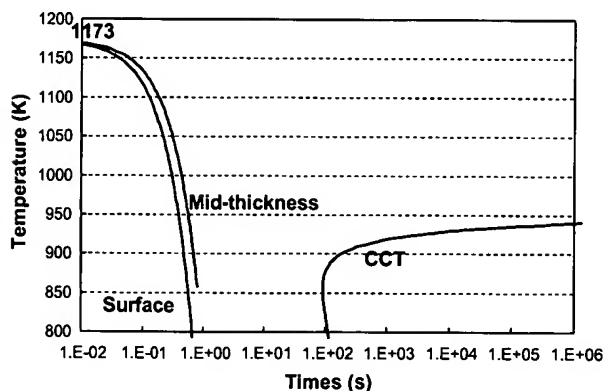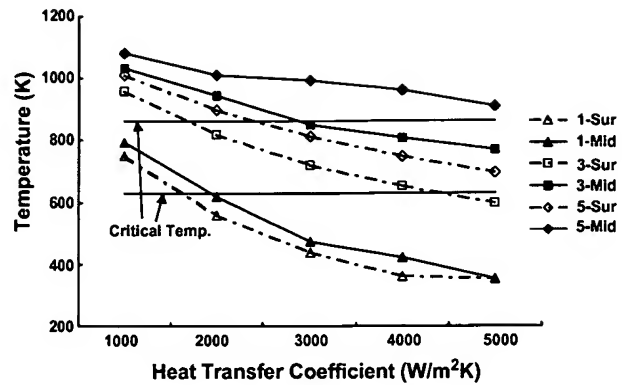

Fig. 3. Variation of surface and mid-thickness temperatures as functions of heat transfer coefficients and rotating speeds of the rolls (1, 3, and 5: rotating speed of rolls, mid.: mid-thickness, sur.: surface).

Table 2
Critical rotating speeds (rpm) of rolls for various heat transfer coefficients (W/m^2 K) for successful fabrication of amorphous alloy sheet

Heat transfer coefficient	1000	2000	3000	4000	5000
Critical rotating speed	0.7–1.3	1.3–2.1	2.0–3.0	2.8–3.6	3.6–3.9

zation kinetics at low temperature is very sluggish. Therefore, it is suggested that two conditions must be met for the successful fabrication of amorphous alloy sheet by twin-roll strip casting; (1) the mid-thickness temperature of the sheet at the roll nip point must be lower than the nose temperature (860 K) of the CCT diagram and (2) the surface temperature of the sheet at the roll nip point must be higher than T_g (630 K).

Temperature profiles for other values of heat transfer coefficient were also calculated (Fig. 3). It shows that the sheet satisfies the above conditions at the following combinations; the rotating speed of 1 rpm for the heat transfer coefficient of 1000 W/m^2 K, the rotating speed of 3 rpm for the heat transfer coefficient of 3000 W/m^2 K, and the rotating speed of 3 rpm for the heat transfer coefficient of 4000 W/m^2 K. The critical rotating speeds that satisfy the above conditions for various values of heat transfer coefficient are shown in Table 2. It shows that the critical rotating speed increases with increasing the value of heat transfer coefficient. This is because a larger value of heat transfer coefficient results in a faster cooling rate, which is associated with a faster rotating speed of rolls.

Fig. 2. Cooling curves of the twin-roll strip cast sheet along with the CCT diagram [22] (rotating speed of 3 rpm).

3. Twin-roll strip casting of bulk amorphous alloys

Based on the above simulation results, two alloys with quite different glass forming abilities (GFAs) were

subjected to twin-roll strip casting; Vit-1 alloy with R_c of ~1 K/s and $Cu_{47}Ti_{33}Zr_{11}Ni_6Sn_2Si_1$ alloy with R_c of ~250 K/s [21]. Twin-roll strip casting were conducted by using horizontal twin-roll strip caster at POSTECH. Details of strip caster are described elsewhere [11]. For the Vit-1 alloy, it was induction melted at 1173 K under an Ar atmosphere. After melting, the molten alloy was transferred into tundish and strip cast in air. Roll gap was 2 mm and the rotating speeds of the rolls were 1 rpm and 3 rpm. Similar conditions were used for the Cu-base alloy, except the melting temperature (1373 K).

As expected from the simulation results, twin-roll strip casting at a slow rotating speed (e.g., 1 rpm) was not successful. The alloy was fully amorphized ahead of roll nip area. Since the temperature of the alloy was well below T_g at roll nip area, the alloy could not be deformed when it passed through the roll nip area, halting the rotation of rolls. On the other hand, twin-roll strip casting at a rotating speed of 3 rpm resulted in a successful fabrication of the alloy sheet. These results indicate that the values of heat transfer coefficient for the present case of twin-roll strip casting are between 3000 and 4000 W/m^2 K. Fig. 4(a) shows the cross-sectional micrograph of the Zr-base alloy sheet produced by twin-roll strip casting at a rotating speed of 3 rpm. It shows that the microstructure of the sheet consists of amorphous matrix with a few polygonal crystalline particles. These polygonal crystalline particles in the sheet were not formed during twin-roll strip cooling, but already existed in the melt [24]. They have a beneficial effect on ductility and toughness of the strip cast Vit-1 alloy [24] and their volume fraction and morphology can be modified by the control of melting processing variables [25].

The above results show that the optimum casting conditions are such that the alloy is in supercooled liquid state ahead of roll nip area. In such case, the alloy can easily be rolled down to the thickness defined by roll gap and the formation of shrinkage defects such as pores can be eliminated by hot rolling effect of twin-roll strip casting. Subsequent air cooling results in the formation of amorphous structure through the thickness of sheet. In addition to the Zr-base amorphous alloy, Cu-base bulk amorphous forming alloy with a high critical cooling rate was also subjected to twin-roll strip casting. This alloy with a nominal composition of $Cu_{47}Ti_{33}Zr_{11}Ni_6Sn_2Si_1$ is known to have a critical cooling rate of 250 K/s [23] and it would be interesting to see whether the sheet with amorphous structure can be produced for this alloy by twin-roll strip casting. The typical microstructure is shown in Fig. 4(b). The microstructure consists of a small volume fraction of crystalline particles in an amorphous matrix, just like the Zr-base amorphous alloy sheet. These results indicate that the twin-roll strip casting can be applied for the fabrication of bulk amorphous alloy sheets with a wide range of

Fig. 4. Microstructures of the bulk amorphous alloy sheets fabricated by twin-roll strip casting; (a) Zr-base and (b) Cu-base.

critical cooling rates. As mentioned previously, twin-roll strip casting considerably reduces production costs compared to conventional processes and thereby can alleviate a limitation of bulk amorphous alloys, i.e., very expensive mostly due to their exotic alloy compositions. This might result in the acceptance of bulk amorphous alloys as affordable structural materials.

4. Summary

The application of twin-roll strip casting allows the fabrication of bulk amorphous alloy sheets. Due to fast solidification rates, twin-roll strip casting is applicable to bulk amorphous forming alloys with a wide range of critical cooling rates. When the twin-roll strip casting conditions are optimized, the produced sheet has no casting defects due to hot rolling effect during twin-roll

strip casting. It is expected that twin-roll strip casting would greatly expand the application of bulk amorphous forming alloys as structural components.

Acknowledgments

References

[1] Inoue A, Shen B, Koshiba H, Kato H, Yavari AR. Nanomaterials 2003;2:661.
[2] Lee B-J, Lee JC, Kim Y-C, Lee H. Met Mater Int 2004;10:467.
[3] Greer AL. Science 1995;267:1947.
[4] Park ES, Kim DH. Met Mater Int 2005;11:19.
[5] Inoue A, Zhang T. Mater Trans JIM 1995;36:1184.
[6] Kim WB, Ye BJ, Yi S. Met Mater Int 2004;10:1.
[7] Szuecs F, Kim CP, Johnson WL. Acta Mater 2001;49:1507.
[8] Kim YC, Na JH, Park JM, Lee JK, Kim WT, Kim DH. Appl Phys Lett 2003;83:3093.
[9] Park SS, Park YS, Kim NJ. Met Mater Int 2002;6:551.
[10] Park YS, Lee SB, Kim NJ. Mater Trans 2003;44:2617.
[11] Park SS, Lee JG, Park YS, Kim NJ. Mater Sci Forum 2003;419(4):599.
[12] Park SS, Kang DH, Bae GT, Kim NJ. Mater Sci Forum 2005;488(9):431.
[13] Park SS, Kim YM, Kang DH, Kim NJ. Mater Sci Forum 2005;475(9):457.
[14] Harms U, Shen TD, Schwarz RB. Scripta Mater 2002;47:411.
[15] Busch R, Masuhr A, Johnson WL. Mater Sci Eng A 2001;304–306:97.
[16] Aydiner CC, Üstündag E, Prime MB, Peker A. J Non-Cryst Solids 2003;316:82.
[17] Guthrie RIL, Isac M, Kim JS, Tavares RP. Metall Mater Trans B 2000;31:1031.
[18] Santos CA, Spim JA, Garcia A. J Mater Process Technol 2000;102:33.
[19] Guthrie RIL, Tavares RP. Appl Math Modell 1998;22:851.
[20] Spinelli JE, Tosetti JP, Santos CA, Spim JA, Garcia A. J Mater Process Technol 2004;150:255.
[21] Peker A, Johnson WL. Appl Phys Lett 1993;63:2342.
[22] Lee SB, Kim NJ. Mater Sci Eng A, accepted for publication.
[23] Park ES, Lim HK, Kim WT, Kim DH. J Non-Cryst Solids 2002;298:15.
[24] Lee JG, Park SS, Lee D-G, Lee S, Kim NJ. Intermetallics 2004;12:1125.
[25] Lee JG, Lee D-G, Lee S, Kim NJ. Metall Mater Trans A 2004;35:3753.